

Final Report for AASERT Grant F49620-92-J-0215.

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Date: September 21, 1995

Parent Award: AFOSR F49620-92-J-0073

Project Title: "Studies of Energy Transfer Processes of Relevance to Chemically
 and Optically Pumped Lasers".

Amount of Funding: 11/1/91 to 10/31/92 \$84,474
 11/1/92 to 10/31/93 \$91,016
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 Equipment supplement \$30,000

Total Funding Provided by AASERT Grant: 66,341

Number of graduate students supported by the parent award: NONE.

Number of students provided for in the AASERT agreement: ONE

Recipient of AASERT award: John E. McCord

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Information concerning the research topic and the recipient of the AASERT award.

AASERT funding was originally requested to permit a US graduate student (Mr. John E. McCord) to work on research problems associated with the chemical oxygen iodine laser (COIL). However, while the grant application was pending, I received a request from the AF Phillips Laboratory (NM) to accept Captain Melvin L. Nowlin into my research group, and supervise the completion of his Ph. D. thesis research. Captain Nowlin had made progress studying COIL related problems at the Phillips Laboratory, and this work was to be included as part of his dissertation. Consequently, he was assigned to work on the iodine energy transfer projects at Emory. Captain Nowlin joined my group in the summer of 1992. In 1994 he was promoted to the rank of Major, and he successfully defended his thesis. Major Nowlin is currently serving as a faculty member at the Air Force Academy at Colorado Springs.

As the iodine energy transfer problems had been designated as Captain Nowlin's dissertation topic, Mr. McCord was assigned to work on a different Air Force supported program (subcontract to Mission Research Corporation under contract F19628-90-C-0025 with the Phillips Laboratory, sponsored by AFOSR under task 2303EP1/PL007). This research involved high resolution spectroscopic studies of diatomic metal oxides and fluorides. Mr. McCord is currently writing his thesis, and is expected to defend in October 1995. After graduation, Dr. McCord will join the Phillips Laboratory (NM) as an NRC post-doctoral fellow.

Publications acknowledging AASERT support

1. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. 158, 40 (1993)
"Laser Spectroscopy of CeO: Characterization and Assignment of States in the 0-3 eV Range".
2. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. 170, 166 (1995)
"Rotation-Electronic Deperturbation Analysis of the 4f6s Configurational States of CeO"
3. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. 164, 27 (1994)
"Laser Spectroscopy of UO: Characterization and Assignment of States in the 0-3 eV Range, with a Comparison to the Electronic Structure of ThO"
4. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Opt. Soc. Am. B. 11, 1 (1994)
"Laser Spectroscopy of LaF: Ligand Field Assignment of the Triplet State Manifold and Analysis of the Hyperfine Structure"

5. L. A. Kaledin, M. G. Erickson, and M. C. Heaven, J. Mol. Spectrosc. **165**, 323 (1994)
"Laser Spectroscopy of GdO: Ligand Field Assignments of $4f^7(^8S)6p-4f^7(^8S)6s$ Transitions"
6. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. **169**, 253 (1995)
"Laser Spectroscopy of YF: Linkage of the Singlet and Triplet State Manifolds"
7. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. **171**, 569 (1995)
"Laser Spectroscopy of ScF: Analysis of Perturbations in the $F^1\Phi-A^1\Delta$ Spectrum"
8. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. Accepted, March 1995
"Laser Spectroscopy of HfO: Linkage of the Singlet and Triplet State Manifolds"
9. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. Accepted, June 1995
"Laser Spectroscopy of TiO: Accurate Term Energies for the Singlet States and Ligand Field Assignments of States in the 0 to 4 eV Range"
10. L. A. Kaledin, J. E. McCord, and M. C. Heaven, J. Mol. Spectrosc. Accepted, July 1995
"Laser Spectroscopy of ZrO: Accurate Term Energies for the Triplet States"

Presentations

John McCord has attended the International Symposium on Molecular Spectroscopy at the Ohio State University for the past three years. He presented the following talks at the meetings:

48th Symposium, June 1993

- RD'04 "Electronic Structure of Actinide Monoxides and their Singly Charged Ions".
- FA01 "Laser Spectroscopy of UO: Characterization , Ligand Field Assignments and Deperturbation Analysis of States in the 0-3 eV Range".
- FD07 "Laser Spectroscopy of LaF: Linkage of the Triplet State Manifold with 0.03 cm^{-1} Accuracy".

49th Symposium, June 1994

- MH03 "Laser Spectroscopy of YF: Linkage of the Singlet and Triplet Manifolds".
- MH04 "Laser Spectroscopy of ScF: Analysis of Perturbations in the $F^1\Phi-A^1\Delta$ System".
- WH14 "Rotation-Electronic Deperturbation Analysis of the $4f6s$ Configurational States of CeO".

Presentations- continued

50th Symposium, June 1995

MH10 "Laser Spectroscopy of HfO: Linkage of the Triplet State Manifolds"

MH11 "Laser Spectroscopy of TiO: Accurate Term Energies for the Singlet State Manifold"

MH12 "Laser Spectroscopy of ZrO: Accurate Term Energies for the Triplet State Manifold"

Technical Accomplishments

A. Introduction and overview

Interest in the properties of molecules that contain heavy atoms (e.g., lanthanides and actinides) has waxed over the past few decades. Curiosity about the basic chemistry of the higher periodic table is partly responsible; practical considerations enter as well. Compounds of the heavier elements are of central importance in the synthesis of new materials with special electronic, magnetic, biological and catalytic properties. In addition, the properties of actinide compounds are relevant to the operation of nuclear reactors and the storage of nuclear waste.

Electronic structure models that are capable of treating heavy elements are needed to provide insights concerning the established properties of known compounds, predictions of the properties of these compounds under extreme conditions, and for the development of new materials with special characteristics. It is also highly desirable to be able to make reliable predictions for systems that are hazardous to study by experimental means. For example, most actinide compounds are short-lived and dangerously radioactive. Knowledge of their spectroscopic and thermodynamic properties is needed for the design of new nuclear fuels, assessment of schemes for recycling spent fuel, predictions of the radiative signatures of atmospheric nuclear blasts, and modeling of catastrophic reactor failure.

In principle, spectroscopic and thermodynamic properties can be derived from accurate electronic structure calculations. However, current *ab initio* methods are too computationally intensive for calculations of large numbers of electronic states for heavy element compounds. Consequently, we have been developing efficient semi-empirical models that are sufficiently accurate for spectroscopic and thermodynamic predictions. These models are based on ligand field theory (LFT), which had been successfully applied to selected lanthanide oxides and fluorides. Accurate spectroscopic data are needed for the development and testing of LFT models. In this research program we expanded the

spectroscopic data base for the oxides and fluorides of lanthanides and related transition metals. For the lanthanides, we examined band systems of the molecules CeO and GdO. LaF was also investigated, as the large hyperfine interactions associated with the La nucleus provided valuable information concerning the configurational assignments of low-lying states. The isoelectronic fluorides of the $(n-1)d^{n-2}s^2$ elements (ScF, YF, and LaF) and the oxides of the $(n-1)d^{n-2}s^2$ elements (TiO, ZrO and HfO) have low-lying excited electronic states that are configurationally related to the lanthanide oxides and fluorides. We recorded new spectra for all of these species, and tested the ability of LFT models to predict the observed electronic structures. The results were very encouraging, as they demonstrate that LFT parameters are transferable (this is essential if the methods are to have any predictive capabilities).

The suitability of LFT models for actinide compounds had not been investigated prior to our work. We explored this issue using UO for two reasons. First, ^{238}U is one of the few actinides that can be handled safely in a university research facility. Second, spectroscopic data for UO and UO^+ are of interest to the radiative signatures group at Hanscom AFB (program contact; Dr. W. A. M. Blumberg). Previous attempts to obtain spectroscopic data for UO^+ had not been successful. Hence, we approached this problem indirectly by recording electronic spectra for UO, analyzing the spectra with LFT models, and then using the models to predict the properties of UO^+ . When we applied LFT to UO and ThO (the only other actinide compound for which there is adequate spectroscopic data) we found that the conceptually appealing "no adjustable parameter" variant of LFT used to treat lanthanide compounds is not sufficient for the actinides. Agreement with the data for UO and ThO was obtained by empirically adjusting the ligand field parameters. Predictions for the electronic structure of UO^+ were made using the adjusted parameters. In ongoing experiments, we are searching for the stronger absorption features predicted by the model. Future theoretical work should address the participation of the metal-centered f and d orbitals in the bonding of ionic actinide compounds, as this is the primary cause for the failure of the "no adjustable parameter" variant of LFT.

B. Summary of Results

1. Laser Spectroscopy of CeO: Characterization and Assignment of States in the 0-3 eV Range. [J. Mol. Spectrosc. **158**, 40-61 (1993)]

Wavelength-resolved fluorescence excitation techniques were used to record thirty one electronic transitions of CeO at a resolution of 0.03 cm^{-1} . All of the sixteen states that correlate with $\text{Ce}^{2+}(4f^6s)\text{O}^{2-}$ were characterized. Ω assignments were unambiguously

determined from observations of the first lines in at least two rotational branches. Accurate term energies and rotational constants were reported. The results were in good accord with a ligand field theory model of the low-lying states.

New assignments were established for four previously observed transitions, and spectra for three new excited states were analyzed. Ligand field theory calculations were used in an attempt to provide configurational assignments for the excited states (including those from previous studies). Twenty two states were tentatively assigned to the $\text{Ce}^{2+}(4f6p)\text{O}^{2-}$ configuration. Twelve others were tentatively assigned to $\text{Ce}^{2+}(4f5d)\text{O}^{2-}$.

2. Rotation-Electronic Deperturbation Analysis of the 4f6s Configurational States of CeO [J. Mol. Spectrosc. 170,166 (1995)]

Rotation-electronic interactions between states of the 4f6s configuration of CeO, mediated by the operator $-B(R)(\hat{J}^+ \cdot \hat{J}_\text{L}^- + \hat{J}^- \cdot \hat{J}_\text{L}^+)$, were calculated. Second-order perturbation theory was used to account for the effect of heterogeneous interactions on the rotation constants within a single configuration. Eigenvectors from a ligand field theory calculation were used to evaluate these interactions. The results demonstrate the capability of the ligand field model to predict electronic-rotational interactions, and they illustrate the value of these interactions for uncovering the atomic-ion quantum numbers that are not readily determined for molecules in the strong spin-orbit coupling limit [Hund's case (c)].

3. Laser Spectroscopy of UO: Characterization and Assignment of States in the 0-3 eV Range, with a Comparison to the Electronic Structure of ThO [J. Mol. Spectrosc. 164, 27 (1994)]

Thirty-three electronic transitions of UO were recorded, and nine low-lying electronic states that correlated with either $\text{U}^{2+}(5f^37s)\text{O}^{2-}$ or $\text{U}^{2+}(5f^27s^2)\text{O}^{2-}$ were characterized. With few exceptions, Ω assignments were unambiguously determined from observations of the first lines in at least two rotational branches. Accurate term energies and rotational constants were reported. Deperturbed constants of $\omega_e=847.4\text{ cm}^{-1}$ and $R_e=1.8382\text{ \AA}$ were determined for the ground state of the $5f^37s$ configuration, and $\omega_e=934.2\text{ cm}^{-1}$ and $R_e=1.7927\text{ \AA}$ for states of the $5f^27s^2$ configuration. Ligand field theory models were used to analyze the low-energy electronic structure of UO. Fitted values of the ligand field parameters $B_0^2(5f)=6586\text{ cm}^{-1}$, $B_0^4(5f)=621\text{ cm}^{-1}$, and $B_0^6(5f)=173\text{ cm}^{-1}$ did not agree with values calculated using a relativistic Dirac-Fock formalism ($B_0^2(5f)=26130\text{ cm}^{-1}$, $B_0^4(5f)=12130\text{ cm}^{-1}$, and $B_0^6(5f)=12020\text{ cm}^{-1}$).

Ligand field theory calculations were also used to provide configurational assignments for the excited states of UO and ThO. Experimentally derived values for

$\Delta B_0^0(nl/n'l')$ parameters were used to predict the electronic structures of UO and UO^+ . The energies of 23 electronic configurations of UO, and 19 electronic configurations of UO^+ , were calculated. The density distributions of the bound states of UO and UO^+ up to their ionization limits were also determined.

4. Laser Spectroscopy of LaF: Ligand Field Theory Assignment of the Triplet State Manifold and Analysis of Hyperfine Structure [J. Opt. Soc. Am. B. 11, 1 (1994)]

High resolution laser induced fluorescence spectra were recorded for eight vibronic bands of LaF. Accurate term energies and rotational constants were derived from these spectra. All of the bands observed belonged to the $e^3\Phi-A^1\Delta$ or $d^3\Phi-a^3\Delta$ transitions. Large hyperfine splittings were observed for the low-J lines of the $a^3\Delta$, $A^1\Delta$ and $e^3\Phi$ states. Ligand field theory calculations and hyperfine constants were used to provide configurational assignments for the excited states of LaF.

5. Laser Spectroscopy of GdO: Ligand Field Assignments of $4f^7(^8S)6p-4f^7(^8S)6s$ Transitions [J. Mol. Spectrosc. 165, 323 (1994)]

Wavelength-resolved fluorescence excitation techniques were used to record three electronic transitions of GdO. Previous analyses of two bands (Yu.N. Dmitriev *et al.*, *Acta Phys. Hung.* 55, 467 (1984) and P. Carette *et al.*, *J. Mol. Spectrosc.* 124, 243 (1987)) were extended with corrections to the assignments of low-J lines.

Improved molecular constants were obtained for the $X^9\Sigma^-$ and $a^7\Sigma^-$ states that correlate with $\text{Gd}^{2+}(4f^7(^8S)6s)\text{O}^{2-}$. A large difference between the spin-orbit coupling constants for $X^9\Sigma^-$ ($\lambda=-0.10353\text{ cm}^{-1}$) and $a^7\Sigma^-$ ($\lambda=-0.64712\text{ cm}^{-1}$) was noted. This difference was ascribed to the fact that the X state is almost pure $f^7(^8S)$, whereas the a state has partial $f^7(^6P)$ character. Analysis of the a state required off-diagonal matrix elements of the spin-orbit interaction, evaluated using sixth-order degenerate perturbation theory, for treatment of non-rotating molecule spin-orbit intervals. In principle, these elements are needed to describe Σ states of septet and higher multiplicity.

Energy intervals reflecting the structure $\text{Gd}^{2+}(4f^7(^8S)6p)\text{O}^{2-}$ were recognized among the excited states of GdO. The results were in good agreement with ligand field theory models for the excited states of lanthanide oxide (LnO) molecules.

6. Laser Spectroscopy of YF: Linkage of the Singlet and Triplet State Manifolds [J. Mol. Spectrosc. 169, 253 (1995)]

Nine electronic transitions of YF were examined. With few exceptions, Ω assignments were determined from observations of the first lines in at least two rotational

branches. Classical studies of rotationally resolved absorption spectra were extended. Accurate term energies and rotational constants were reported. Ligand field theory calculations were used to suggest electronic configurations for the excited states of YF.

7. Laser Spectroscopy of ScF: Analysis of Perturbations in the $F^1\Phi - A^1\Delta$ Spectrum [J. Mol. Spectrosc. **171**, 569 (1995)]

The 0-0 and 1-1 bands of the ScF $F^1\Phi - A^1\Delta$ transition were investigated at high resolution. The $\Omega=3 - \Omega=2$ assignment was verified, and accurate term energies and rotational constants were determined. Perturbations in the $F^1\Phi$ state, caused by interactions with the $h^3\Pi_2$ state, were analyzed. Using a method based on Franck-Condon factors, the vibrational numbering in the perturbing $h^3\Pi_2$ state was estimated. Parameters determined from the spectroscopic analyses were in good agreement with the results from the *ab initio* calculations of Langhoff, Bauschlicher, and Partridge (*J. Chem. Phys.*, **89**, 396 (1988)).

8. Laser Spectroscopy of HfO: Linkage of the Singlet and Triplet State Manifolds [J. Mol. Spectrosc. Accepted, March 1995]

Reinvestigation of the HfO 5698 Å band and reexamination of existing spectroscopic data provided strong indications that transitions formerly assigned to the $B^1\Pi - X^1\Sigma^+$ and $A^1\Sigma^+ - X^1\Sigma^+$ transitions should be reassigned to $b^3\Pi_1 - X^1\Sigma^+$ and $b^3\Pi_0^+ - X^1\Sigma^+$, respectively. With these revisions the energies of several triplet states were determined relative to the ground state.

Energy intervals reflecting the structure of the $Hf^{2+}(5d6s)$ free-ion were recognized among the complex of the low-lying states. LFT predictions were used to assign many of the experimentally observed states of HfO.

9. Laser Spectroscopy of TiO: Accurate Term Energies for the Singlet States and Ligand Field Assignments of States in the 0 to 4 eV Range [J. Mol. Spectrosc. Accepted, June 1995]

Laser excitation spectra were recorded for the (2,0) band of the $C^3\Delta_3 - a^1\Delta$ transition, and the (2,3) and (2,4) bands of the $C^3\Delta_3 - X^3\Delta_3$ electronic transition of TiO. These data were combined with a previous high-resolution analysis of the $C^3\Delta - X^3\Delta$ system (T. Gustavsson, C. Amiot, and J. Verges, *J. Mol. Spectrosc.* **145**, 56-65 (1991)) to obtain accurate term energies for the singlet states of TiO. The term energy obtained for the first excited $a^1\Delta$ state was $T_0(a^1\Delta) = 3444.367 \pm 0.020 \text{ cm}^{-1}$. This value

differed significantly from the previously derived value of $T_0(a^1\Delta) = 3448.33 \pm 0.04 \text{ cm}^{-1}$ (A.I. Kobylyanskii, A.N. Kulikov, and L.V. Gurvich, *Opt. Spectrosc.* **54**, 254-255 (1983)). Ligand field theory models were used to analyze the electronic structures of TiO, TiS, and TiCl^+ .

10. Laser Spectroscopy of ZrO: Accurate Term Energies for the Triplet States [J. Mol. Spectrosc. Accepted, July 1995]

Rotationally resolved spectra were taken for the (0,0) bands of the satellite $e^3\Pi_1 - a^3\Delta_1$ and $e^3\Pi_2 - a^3\Delta_2$ transitions of ZrO. These data were combined with previous high resolution analyses of the ZrO β -system (B. Simard *et al.*, *Faraday Discuss. Chem. Soc.* **86**, 163-180 (1988)) and with an analysis of the intercombination $e^3\Pi_1 - X^1\Sigma^+$ transition (P.D. Hammer and S.P. Davis *Astrophys. J. Lett.* **237**, 51-53 (1980)) to obtain accurate term energies for the triplet states of $^{90}\text{Zr}^{16}\text{O}$. Ligand field theory calculations were used to determine electronic configurations for the excited states of ZrO.

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) Spectroscopic properties of gas phase transition metal oxides and fluorides were investigated using experimental and theoretical techniques. High resolution electronic spectra were recorded for the molecules UO, CeO, GdO, TiO, ZrO, HfO, ScF, YF, and LaF. These data were used to test and develop ligand field theory models for the low-lying electronic states of lanthanide and actinide compounds. Ligand field calculations were used to predict the properties of the elusive UO ⁺ ion. DTIC QUALITY INSPECTED 8				
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